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Microwave-enhanced cross-coupling of allyl chlorides with vinyltrifluoroborates

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Abstract—The allylation of potassium alkenyltrifluoroborates with allyl chloride via a palladium catalyzed cross-coupling reaction occurs rapidly under microwave irradiation. The allylation reaction produces 1,4-pentadienes in high yields.

Palladium catalyzed cross-coupling reactions between organoboron compounds and organic halides are powerful tools for carbon–carbon bond formation.[1] A wide variety of boron reagents, including trifluoroborates, can be utilized in these Suzuki–Miyaura reactions.[2] Trifluoroborates can easily be prepared and are remarkably stable, yet they are particularly useful since they are quite reactive.[3]

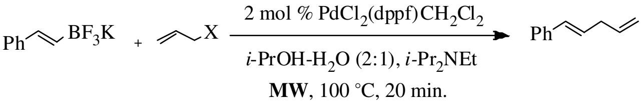
We have been investigating the use of microwave irradiation as an alternative to thermal heating in reactions including boron derivatives.[4] Organic syntheses involving microwave systems, in contrast to classic thermal conditions, provide the opportunity to complete complex reactions in a course of minutes, as opposed to hours when thermal conditions are used.[5]

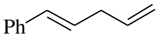
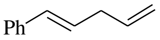
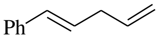
We recently reported the use of microwaves for cross-coupling reactions involving potassium aryltrifluoroborates and vinyltrifluoroborates.[4a,b] We now wish to describe the results of a study focused on the coupling of allyl halides with potassium vinyltrifluoroborates. As shown in Table 1, allyl chloride produces the highest yields of the desired products. This study was initiated by allowing potassium *trans*-2-[4-(trifluoromethyl)-phenyl]vinyltrifluoroborate to react with allyl halides in the presence of palladium catalyst. No carbon–carbon bond formation occurred in the absence of palladium. $PdCl_2(dppf){\cdot}CH_2Cl_2$, $Pd_2dba_3{\cdot}CHCl_3$/dppf, Pd_2dba_3/(*o*-tolyl)$_3$, $Pd(OAc)_2$/dppf and $Pd(OAc)_2$ were examined as potential catalysts. Solvents such as tetrahydrofuran and *tert*-amyl alcohol were also evaluated. Cesium carbonate, potassium carbonate and triethylamine were evaluated as potential bases. The organotrifluoroborates were readily prepared from the corresponding boronic acids.[3a]

A series of allyl chlorides were then allowed to react with various substituted potassium vinyltrifluoroborates (Table 2). A catalyst loading of 2 mol % $PdCl_2$(dppf)-CH_2Cl_2, along with 3.0 equiv of Hünig's base (*i*-Pr_2NEt), in isopropanol/water (2:1), at 100 °C under microwave irradiation was found to provide the coupled products in good to excellent yields.

The reactions are rapid and straightforward. In a typical experiment, the organotrifluoroborates (0.50 mmol) and palladium catalyst (0.01 mmol) are placed in an argon

Table 1. Microwave-enhanced cross-coupling reactions of potassium phenylvinyltrifluoroborate with allyl halides



Entry	X	Product	Yield%[a]
1	I		55
2	Br		65
3	Cl		81

[a] All yields are of pure products isolated by silica gel chromatography.

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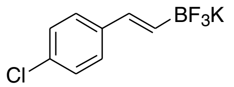
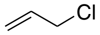
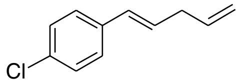
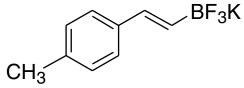
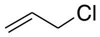
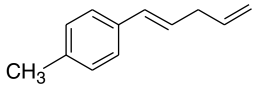
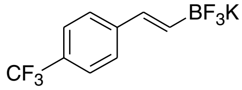
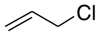
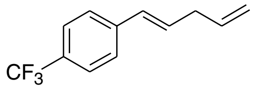
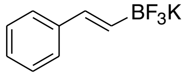
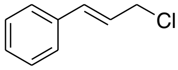
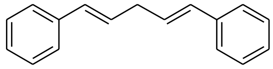
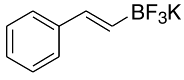
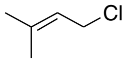
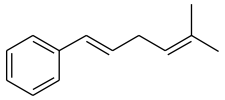
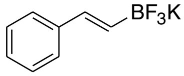
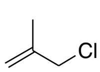
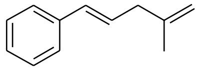
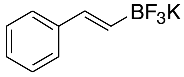
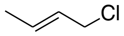
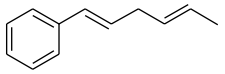
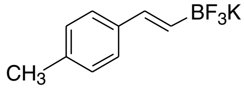
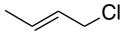
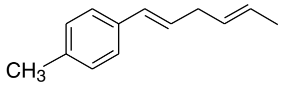
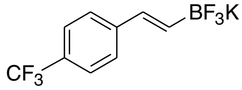
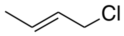
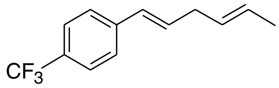
Table 2. Microwave-enhanced cross-coupling reactions[a]

Entry	Alkenyl trifluoroborate	Allylating agent	Product	Yield%[b]
1				71
2				79
3				89
4				46
5				54
6				64
7				51
8				81
9				75

[a] All reactions were run in *i*-PrOH–H_2O (2:1) at 100 °C for 20 min.

[b] Isolated yields.

flushed pyrex test tube. The aryl halide (0.50 mmol) is then added along with diisopropyl ethyl amine (1.5 mmol) and 5 mL of isopropanol/water (2:1). The tube is capped with a plastic septum, placed in a CEM microwave unit and allowed to react at 100 °C for 20 min. The product is isolated by adding water (~25 mL) and ether (~35 mL), the ether layer separated, and the organic phase dried over anhydrous sodium sulfate. The ether solution is filtered, and the product isolated by column chromatography using hexane/ethyl acetate (100/1). In some reactions, the conjugated diene by-product was observed (5%) which is readily removed by chromatography.

Acknowledgements

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